16TH GROUP ELEMENTS

- Called 'Chalcogens' (only O, S, Se, Te) due to their ore forming abilities

Chalcogens:
- ${}_8O$ - $[He]2s^2 2p^4$
- ${}_{16}S$ - $[Ne]3s^2 3p^4$
- ${}_{34}Se$ - $[Ar]3d^{10}4s^2 4p^4$
- ${}_{52}Te$ - $[Kr]4d^{10}5s^2 5p^4$

GEC = ns^2np^4

- ${}_{84}Po$ - $[Xe]4f^{14}5d^{10}6s^2 6p^4$ → Radioactive element with $t_{1/2}$ = 13.88 day
- ${}^{Uuh}_{116}$ - $[Rn]5f^{14}6d^{10}7s^2 7p^4$

Relative abundance

O > S > Se > Te

Oxygen:

- Air contains 20.946 % by volume of O_2.
- 46.6% of O_2 is present in combined state in earth's crust

Sulphur:

- 0.03 - 0.1 % by weight of sulphur is present in free state as well as in combined state
- $Na_2SO_4 \cdot 10H_2O$ - (Glauber's salt)
  $MgSO_4 \cdot 7H_2O$ (Epsom salt)
  $CaSO_4 \cdot 2H_2O$ (Gypsum)
  HgS (Cinnabar)
  $BaSO_4$ (Barytes)
  $PbSO_4$ (Anglesite)
  PbS (Galena)
  ZnS (Zinc Blende)
  Ag_2S (Argentite

- H_2S - from volcanic gases

- Se, Te are available as metal selenites, tellurites in sulphide ores
- Po is obtained as a disintegration product of U & Th.

2. Physical state:

O → gas

S, Se, Te, Po → solids

3. Metallic nature:

O, S → non-metals

Se, Te → metalloids

Po → metal

4. Covalent radius

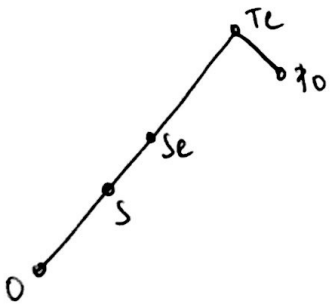
O —Inc→ Po

Ionic radius

O^{2-} —dec→ Po^{2-}

5. Density: O —Inc→ Po

6. MP & BP



- MP & BP of Te > Po
- Po has lesser MP, BP than expected due to inert pair effect so only 4 e^- (p-electrons) take part in metallic bond
- In Te, 6 valence e^- are involved in covalent bond formation.

. O & S greatly differ in their MP & BP values:

Reason: O_2 is a diatomic gas while S_8 is octatomic solid.

7. IP: $O \xrightarrow{\text{Dec}} Po$

. The higher IP of Oxygen is due to its smaller size

. IP of N > O

8. EN (on Pauling's scale)

O	S	Se	Te	Po
3.5	2.58	2.55	2.01	1.78

9. Electron affinity:

S > Se > Te > Po > O

· EA of O < S

Reason: Due to small size of oxygen, there exist greater inter electronic repulsions between e^- already present and the added e^-

$$O + e^- \longrightarrow O^- \qquad \Delta H = -ve$$
$$O^- + e^- \longrightarrow O^{2-} \qquad \Delta H = +ve$$
$$O + 2e^- \longrightarrow O^{2-} \qquad \Delta H = +ve$$

10. Catenation

S > O > Se > Te

Reason: Bond energy of S-S > O-O > Se-Se > Te-Te

· Bond energy of O-O < S-S

Reason: Due to the repulsions among oxygen atoms which weakens the bond.

(O is smaller in size so O-O bond length is shorter)

- Oxygen can form H_2O_2
- S forms polysulphides H_2S_n

11. Atomicity

O ⟶ Diatomic (O_2)

S, Se, Te ⟶ Octa atomic (S_8, Se_8, Te_8)

P_o ⟶ Monoatomic (P_o)

12. Multiple bond formation

- Oxygen forms strong pΠ-pΠ bonds

  Reason: Small size & high EN

- pΠ-pΠ bond forming tendency decreases down the group.

  CO_2 (stable)

  CS_2 (less stable)

  CSe_2 (polymerizes instead of forming double bonds)

  CTe_2 (Non existent)

- Oxygen cannot form pΠ-dΠ bonds.

  Reason: Absence of d-orbitals

- S, Se, Te, P_o cannot form effective pΠ-pΠ bonds.

  Reason: Due to large size, p-orbitals are more dispersed.

- S, Se, Te, P_o form stronger pΠ-dΠ bonds.

  Reason: Presence of d-orbitals.

- pΠ-dΠ bond strength in $SiO_3^{2-} < PO_4^{3-} < SO_4^{2-} < ClO_4^-$

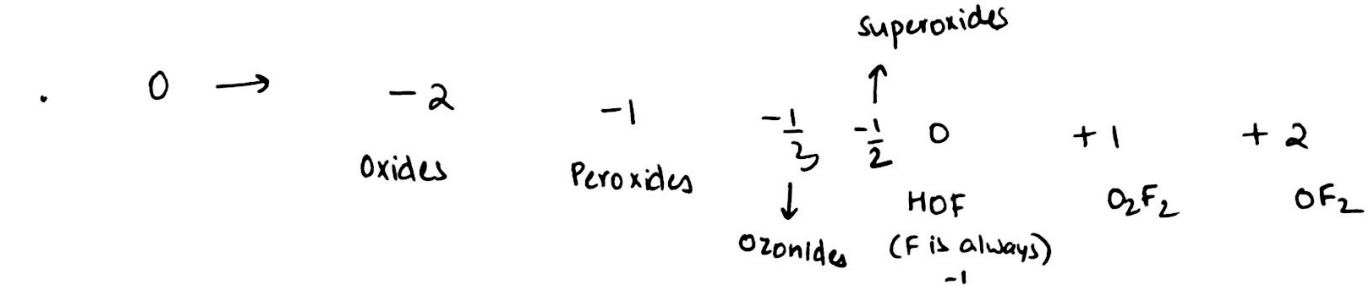
If pΠ-dΠ bond strength decreases, tendency to polymerize increases:

Tendency to polymerize : $SiO_3^{2-} \gg PO_4^{3-} > SO_4^{2-} > ClO_4^-$

↓

Don't polymerize

13. Oxidation states



- S, Se, Te ⟶ −2, +2, +4, +6
- Po ⟶ −2, +2, +4

- The stability of +4 state increases while +6 state decreases down the group.

  Reason: Increase of inert pair effect.

- Stability of $Po^{+6} \ll Po^{+4}$ due to inert pair effect.

  ∴ PoO_3 is powerful oxidant.

- Oxidising power of $PoO_3 > TeO_4^{2-} > SeO_4^{2-} > SO_4^{2-}$

14. Covalency:

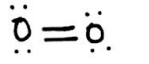
- Max. covalency of oxygen = 4
- Max. covalency of other elements = 6

15. Allotropy

a) Allotropes of oxygen

i) Dioxygen (O_2):

- Colourless gas
- Stable
- Paramagnetic ($\pi^*_{2py} = \pi^*_{2pz}$)
- BP = 90 K
- Liq. O_2 is pale blue
  Solid O_2 - blue



$\pi^*_{2py} \equiv \pi^*_{2pz}$

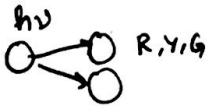
Spin multiplicity = $2|S|+1$

(2nd ES)	O_2^*	↑ ↓	1 (singlet)
(1st ES)	O_2^*	↑↓	1 (singlet)
(G.S)	O_2	↑ ↑	3 (triplet)

Reason: Transition from triplet ground state to excited singlet state.

- In liq/solid O_2, a single photon strikes two O_2 molecules simultaneously and promotes them to excited state by the absorption of Red, Yellow, Green wavelengths.

  During de-excitation, the complementary colour blue is seen.



- Gaseous Oxygen is colourless since triplet to singlet transitions are forbidden.

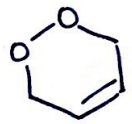
- Singlet O_2 is more reactive.

$$O_2 \xrightarrow[\text{Photo sensitizer (Fluoroscien (or) Methylene blue (or) Poly hydrocarbon)}]{h\nu} O_2^*$$

(normal) (singlet)

Singlet O_2 is obtained by photosensitization of normal oxygen.

- Singlet O_2 is more reactive than normal oxygen.

- $CH_2=CH-CH=CH_2 + O_2^* \longrightarrow$ 

(1,4 addition)

- $CH_3-CH=CH-CH_3 + O_2^* \longrightarrow CH_3-\underset{|}{\overset{O-O}{CH}}-\underset{|}{\overset{O-O}{CH}}-CH_3 \longrightarrow 2CH_3CHO$

- O_2^* is involved in biological oxidation.

ii) Ozone (O_3)

- Deep blue gas

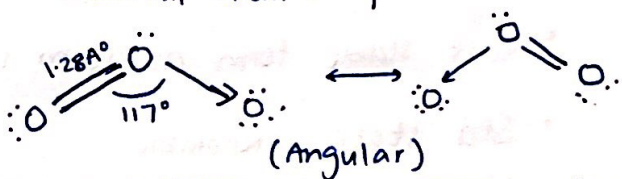
$\mu \neq 0$

$BO = \frac{2+1}{2} = 1.5$

$BL = 1.28\ A^0$

$BA = 117^\circ$

central atom = sp^2 with 1 lp



(Angular)

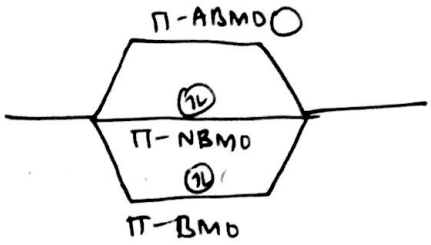
π-system – $3c-4e^-$

since $4e^-$ are oscillating among 3 atoms

Reason: It strongly absorbs the red wavelengths 557 & 602 nm.

- It shows strong absorption even in UV region.
- It occurs in stratosphere.
- Unstable thermodynamically.
- Angular molecule with some net dipole moment.
- ~~Paramagnetic~~
- Diamagnetic (O_3) while O_3^- or KO_3 is paramagnetic.

- π-system → $2c - 4e^-$



b) Allotropes of Sulphur

i) Rhombic / Octahedral / α- Sulphur

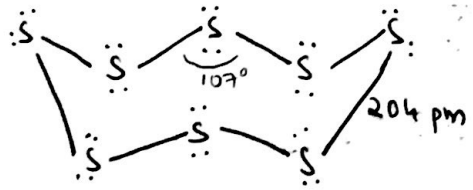
- Pale yellow solid
- Concists of S_8 units
- MP = 385·6 K
- Density = 2·06 g/cc
- Most stable form at room temp.
- Std state = Rhombic

Rolls-S + CS_2 $\xrightarrow{\text{evaporation}}$ Rhombic S

$\Delta H^\circ_{f\,(rhombic)} = 0$

Thermodyna-mically Most stable state = Rhombic

- Insoluble in water
- Soluble to some extent in alcohol, ether & benzene.
- Highly soluble in CS_2.



Each S has 2 lp

Puckered ring / crown shape

S–S = 204 pm

∠SSS = 107°

ii) Monoclinic / Prismatic / β - Sulphur

Prep:

- Molten S is cooled in a china dish until crust formation takes place.
- Then, 2 holes are made in the crust. Then the molten sulphur is poured out.
- The needle like crystals left after removal of crust is monoclinic sulphur.

Properties:

- Dirty yellow solid.
- Consists of S_8 units.
- MP = 393 k
- Density = 1.98 g/cc
- Stable above 369 K (Transition temp. of S)
- Insoluble in water.
- Soluble in CS_2.

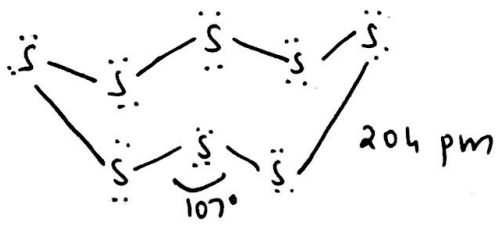
$$\alpha\text{-Sulphur} \underset{< 369\ K}{\overset{> 369\ K}{\rightleftharpoons}} \beta\text{-sulphur}$$

Transition temp. of S :

Above 369 K, β-Sulphur is stable.

Below 369 K, α-sulphur is stable.

At 369K, both α & β sulphurs exist in eq. with each other. This temp. is called transition temp.

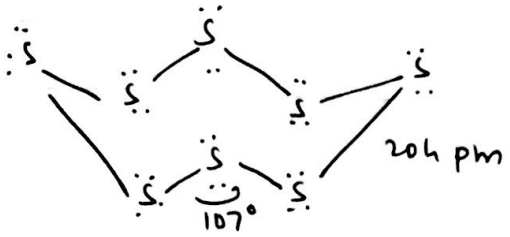


iii) γ- Monoclinic (or) γ- Sulphur

- Nacreous form (looks like mother of pearl) - Brownish yellow
- Consists of S_8 units
- Density = 2.16 g/cc
- Insoluble in water
- Soluble in CS_2
- Unstable

Prep:

- By chilling hot conc. Sulphur in organic solvents (CS_2 or alcohol) or toluene



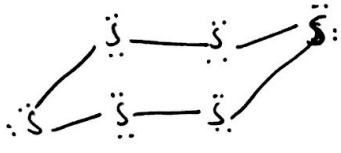
- Density of γ > α > β Sulphur

iv) Engel Sulphur / E-Sulphur / Cyclo S_6

Prep:

1. $H_2S_4 + S_2Cl \longrightarrow S_6 + 2HCl$
2. $Na_2S_2O_3 + HCl \xrightarrow[\text{with toluene}]{\text{Extracted}} S_6$ (conc)

- Consists of S_6 units in chair conformation.



S-S = 205.7 pm

∠SSS = 102.2°

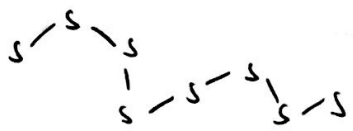
- Unstable
- Soluble in CS_2

- $H_2S_8 + S_2Cl_2 \longrightarrow S_{10} + 2HCl$
- $H_2S_8 + S_4Cl_2 \longrightarrow S_{12} + 2HCl$

v) Plastic / χ - Sulphur

Amorphous form

- Obtained by pouring liquid / molten sulphur in water.
- Consists of spiral chains.
- Rubber - like elastic mass.
- Insoluble in H_2O & CS_2
- Amorphous form, so no sharp MP.
- Unstable
- Upon standing, reverted back to α- form.



vi) Colloidal Sulphur

Prep:

- $H_2S + SO_2 \longrightarrow S + H_2O$ (colloidal)
- HNO_3 (conc) $+ H_2S \longrightarrow S$ (colloidal) $+ NO_2 + H_2O$
- $Na_2S_2O_3 + HCl$ (dil) $\longrightarrow S\downarrow + SO_2 + NaCl + H_2O$

- Colloidal sulphur is multimolecular colloid.

  Reason: Each colloidal particle consists of several S_8 units.

vii) Milk of Sulphur

$$Ca(OH)_2 + C \longrightarrow \underbrace{CaS_5 + CaS_2O_3}_{\downarrow \text{dil HCl}} + H_2O$$

$$S\downarrow \text{ (milk of sulphur)} + CaCl_2 + H_2O$$

Other forms:

- Laminar
- Rubber-like
- Commercial form is crystex.

$$S_{(s)} \xrightarrow{\Delta} \text{Molten sulphur} \longrightarrow S_8 \text{ rings broken to diradical } (\cdot S\cdot) \text{ (At 160°)}$$

$(\cdot S\cdot)$ $\downarrow$ upto 200°C

Long chain (viscosity ↑, physical properties change) (vapours contain S_2 gas)

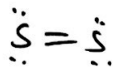
Long chain $\xrightarrow{444°C}$ Smaller chains (viscosity ↓)

- When S is heated, it turns into molten state. When it is heated to 160°C the S_8 rings are broken to form diradicals $(\cdot S\cdot)$
- The diradicals combine to form long chains upto 200°C during which viscosity increases and physical properties change. The vapours at 200°C also contain 1-2% S_2 molecules

from 200°C to 444°C, the long chains are broken into smaller chains so viscosity decreases.

Above 1000 K (600°C as per JD Lee), the predominant species is S_2.

- S_2 gaseous molecules are stable upto 2200°C
- Structure of S_2 similar to that of O_2



  - S_2 = Blue colour
  - Paramagnetic ($\pi^*_{3py^1} \equiv \pi_{3pz^1}$)

c) Allotropes of Se

3 Red + 2 Grey + 1 Amprphous

d) Allotropes of Te — No allotropy - only 1 form.

- Te has only one form which is isomorphous with grey metallic form of Se.

e) Allotropes of Po

- α- Po (cubic)
- β- Po (Rhombic)

Hydrides

H_2O H_2S H_2Se H_2Te H_2Po

Prep:

- $2H_2 + O_2 \longrightarrow 2H_2O$
- $FeS + \underset{HCl\ (dil)}{H_2O} \longrightarrow H_2S + FeCl_2$
- $ZnSe + 2HCl \longrightarrow H_2Se + ZnCl_2$
- $Al_2Te_3 + 6H_2O \longrightarrow 3H_2Te + 2Al(OH)_3$
- $Mg\text{-}Po + 2HCl \longrightarrow H_2Po + MgCl_2$

Structural aspects

H_2M type covalent hydrides

Angular

H_2O	H_2S	H_2Se	H_2Te
$104°30'$	$92°$	$91°$	$90°$
$\downarrow$			
sp^3		Pure-p	

- In H_2O molecule, oxygen atom is in sp^3 hbd. Due to lp-lp & lp-bp repulsions, bond angle decreases to $104°30'$
- In H_2S, H_2Se, H_2Te, H_2Po, bond angles are close to $90°$ since pure p-orbitals involve in bonding.

- Bond angle decreases from H_2O to H_2Te since EN decreases.

General properties:

- **Nature:**

  H_2O → non-toxic

  H_2S, H_2Se, H_2Te, H_2Po ⟶ Toxic

- **Physical state:**

  H_2O ⟶ liquid (H-bonds)

  H_2S, H_2Se, H_2Te, H_2Po ⟶ gas

- Covalent nature : $H_2O \xrightarrow{Inc} H_2Po$ (Polarity decreases)

  Ionic nature : $H_2O \xrightarrow{Dec} H_2Po$

- Thermal stability: $H_2O \xrightarrow{Dec} H_2Po$

  Reason: M-H bond energy decreases

- More -ve, Less -ve
  H_2O, H_2S are exothermic compounds (ΔH_f = -ve)

  H_2Se, H_2Te are endothermic compounds (ΔH_f = +ve)
  Less +ve, More +ve

- **Acidic nature**

  Acidic strength : $H_2O \xrightarrow{Inc} H_2Po$

  Reason: M-H bond-energy decreases.

- Ka of $H_2O < H_2S < H_2Se < H_2Te$ ($ka \uparrow$, $pka \downarrow$)
  (Acidic strength)

- CB strength $OH^- > HS^- > HSe^- > HTe^-$ ($k_b \downarrow$, $pk_b \uparrow$)

CA strength : $O^{2-} < S^{2-} < Se^{2-} < Te^{2-}$ ($K_a \uparrow$, $pK_a \downarrow$)

- H_2S is twice as soluble as CO_2
- H_2S dissolves in aq. NH_4OH

$$NH_4OH + H_2S \longrightarrow NH_4HS + H_2O$$

but NOT $(NH_4)_2S$

- Alkali metal sulphide aq. solns are strongly alkaline due to hydrolysis.

$$Na_2S + H_2O \rightleftharpoons NaHS + NaOH$$

- Reducing nature

$$H_2O \xrightarrow{Inc} H_2Po$$

Reason: Bond energy decreases.

- Hydrogen bond forming tendency : $H_2O \xrightarrow{Dec} H_2Po$

  Reason: Polarity of bond decreases and size of central atom increases.

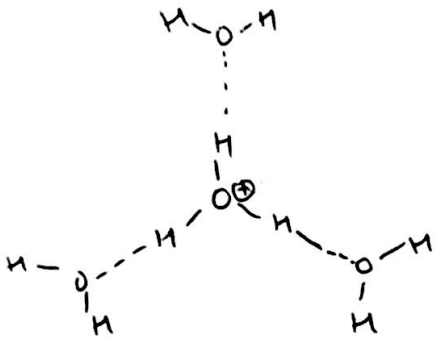
- H_2O is a levelling solvent.

  All strong acids have same strength in H_2O (i.e. H_3O^+)

  bases (i.e. OH^-)

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

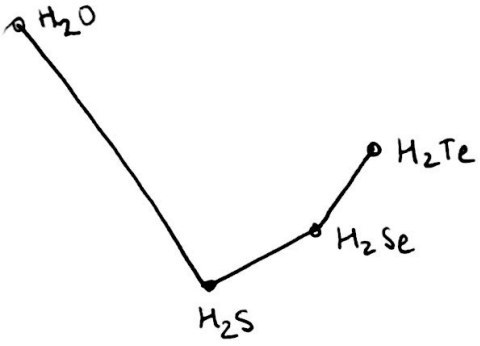
- Max no. of H-bonds = 4 in ice (ice has wurtzite structure)
- According to recent studies, H^+ is known to exist as $(H(H_2O)_4)^+$ or $H_9O_4^+$



$H_9O_4^+$

No. of H-bonds in $H_9O_4^+$ = 3

BP & MP



The abnormally higher MP & BP of H_2O is due to H-bonding

- **Volatility**

Volatility $\alpha \frac{1}{BP}$

Volatility of $H_2S > H_2Se > H_2Te > H_2O$

Oxides:

1. **Monoxides** (MO)

   SO, TeO, PoO

   SeO is non-existent

2. **Dioxides** (MO_2) $MO_2 \rightarrow$ Reductants

   - SO_2 – gas
     - acidic
     - soluble in water ($SO_2 + H_2O \rightarrow H_2SO_3$)

   - SeO_2 – volatile solid
     - acidic
     - soluble in water ($SeO_2 + H_2O \rightarrow H_2SeO_3$)

   - TeO_2 – crystalline solid & ionic
     - amphoteric
     - insoluble in water
     - soluble in acids & alkalis
       - $TeO_2 + NaOH \rightarrow Na_2TeO_3$ (tellurate)
       - $TeO_2 + HNO_3 \rightarrow HNO_3 \cdot 2TeO_2$ (or) $Te_2O_3(OH)NO_3$ (addition compound)

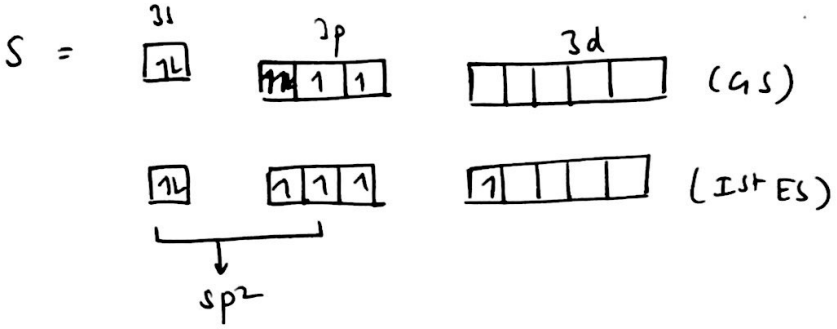
   - PoO_2 – crystalline ionic solid
     - amphoteric
     - insoluble in water

MO_2 – reducing agents

- Acidic nature : $SO_2 > SeO_2 > TeO_2 > PoO_2$
- Thermal stability : $SO_2 > SeO_2 > TeO_2 > PoO_2$
- Reducing nature : $SO_2 > SeO_2 > TeO_2 > PoO_2$

SO_2

- Colourless gas



← In gas phase

Angular

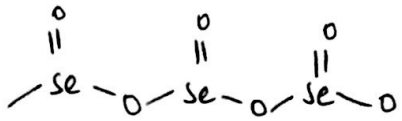
(1 pπ-pπ + 1 pπ-dπ)

$\mu = 1.63$ D

- In solid state, it exists as molecular solid
- It behaves as both LA and LB

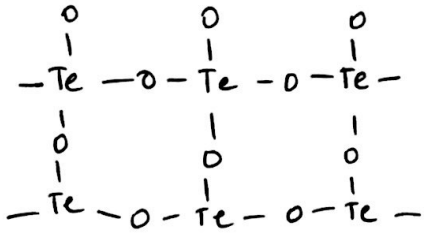
SeO_2 :

- Structure is similar to SO_2 in gas phase
- Exists as a linear polymer in solid state



TeO_2:

- A network solid



3. Trioxides (MO_3)

MO_3 - oxidants

- SO_3 - volatile solid
  - acidic
  - soluble in water

    $SO_3 + H_2O \rightarrow H_2SO_4$

- SeO_3 - polymeric solid
  - acidic
  - soluble in water ($SeO_3 + H_2O \rightarrow H_2SeO_4$)

- TeO_3 - polymeric solid
  - acidic
  - soluble in water

    $TeO_3 + H_2O \rightarrow H_6TeO_6$ (or) $Te(OH)_6$

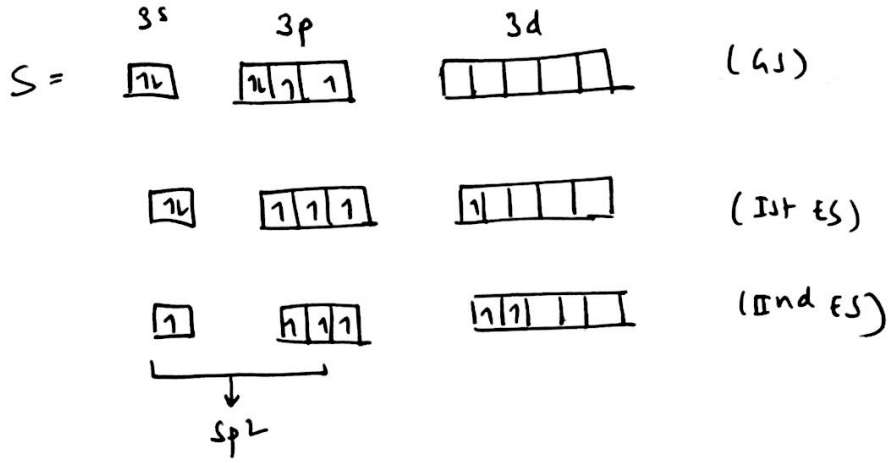
    Telluric acid

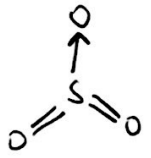
MO_3 — good oxidants

Oxidising power : $SO_3 < SeO_3 < TeO_3 < PoO_3$

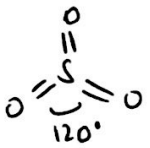
- Thermal stability : $SO_3 > SeO_3 > TeO_3 > PoO_3$
- Acidic strength : $SO_3 > SeO_3 > TeO_3 > PoO_3$

SO_3





(or)



In gas phase

BO = 3/3 = 1.6

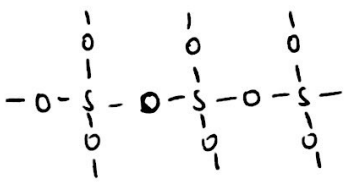
Planar triangular

(1 pπ-pπ + 2 pπ-dπ)

$\mu = 0$

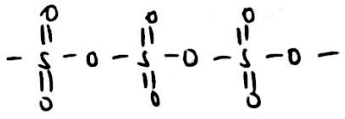
- Lewis acid
- SO_3 in solid state exists in 3 forms: α, β, γ

- **α-SO_3 (cross linked)**



cross linked

- **β-SO_3 (linear)**

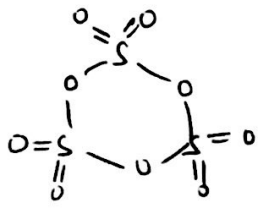


(linear)

(CrO_3 - same structure)

*. CrO_3 has similar ~~properties~~ structure as ~~of~~ β-SO_3

- **γ-SO_3 (cyclic trimer)**

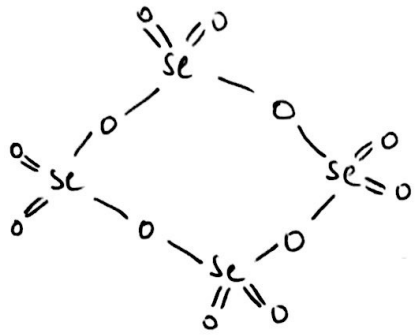


MP of $\alpha > \beta > \gamma$

- SO_3 can act as Lewis acid.

SeO_3

- In solid state exists as tetramer (Se_4O_{12})

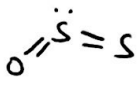


TeO_3

- Cross-linked / network solid.

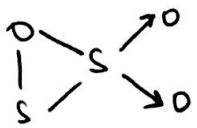
- Sulphur forms SO (colourless gas) & S_2O (colourless gas)

$$SO_2 + 3S \xrightarrow[\text{discharge}]{\text{silent electric}} 2S_2O$$



S_2O is highly reactive & attacks metals and alkalis and undergoes polymerization.

- S_2O_3 (bluish green solid)



- SO_2 (colourless gas)
- SO_3 (volatile solid)
- S_2O_7 (volatile liquid)

$$2SO_2 + \frac{3}{2}O_2 \xrightarrow[\text{discharge}]{\text{silent electric}} S_2O_7$$

16TH GROUP ELEMENTS (contd.)

$$S_2O_7 \xrightarrow{\Delta} 2SO_3 + \tfrac{1}{2}O_2$$

$$S_2O_7 + H_2O \longrightarrow H_2S_2O_8$$

- SO_4 (white solid)

- Cyclo S_{6-10} (in CS_2 / CH_2Cl_2) + CF_3COOOH (peroxy acid) $\xrightarrow{-10 \text{ to } -30^\circ C}$ $S_{6-10}O$ (orange yellow solid) + CF_3COOH

HALIDES

1. Monohalides (M_2X_2)

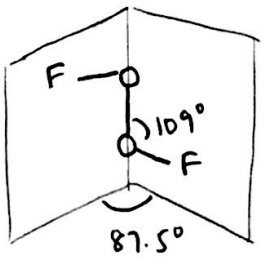
O_2F_2

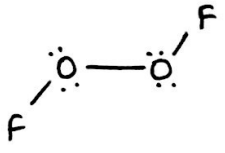
S_2F_2, S_2Cl_2, S_2Br_2

Se_2Cl_2, Se_2Br_2

- $O_2 + F_2 \xrightarrow[\text{discharge}]{\text{silent electric}} O_2F_2$

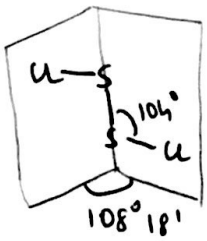
O_2F_2 has open book structure (like H_2O_2)

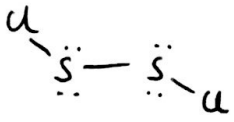




Hbd of O = sp^3

- $2S + Cl_2 \xrightarrow{\Delta} S_2Cl_2$





Hbd of S = sp^3

- These monohalides undergo disproportionation on hydrolysis or upon heating

  - $Se_2Cl_2 \xrightarrow{\Delta} Se + SeCl_4$
  - $2S_2F_2 + 2H_2O \longrightarrow SO_2 + 3S + 4HF$
  - $2S_2Cl_2 + 2H_2O \longrightarrow SO_2 + 3S + 4HCl$
  - $H_2Sn + 2S_2Cl_2 \longrightarrow S_{(n+4)}Cl_2 + 2HCl$

- S_2Cl_2 is used in the manufacture of mustard gas

$$S_2Cl_2 + 2CH_2{=}CH_2 \longrightarrow Cl\overset{\beta}{C}H_2\overset{\alpha}{C}H_2 - S - \overset{\alpha'}{C}H_2\overset{\beta'}{C}H_2Cl + S$$

(β,β'-dichloro diethyl thio ether)

S_2Cl_2 is used in vulcanization of rubber.

Dihalides (MX_2)

- $NaOH + F_2 \longrightarrow OF_2 + NaF + H_2O$

OF_2, OCl_2, OBr_2

SF_2, SCl_2
(dark red liq.)

$TeCl_2$, $TeBr_2$, TeI_2

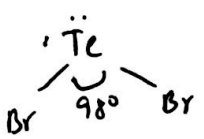
$PoCl_2$, $PoBr_2$, PoI_2 (unstable)

Prep:

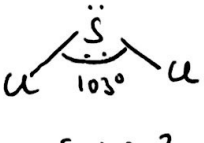
$$2S + Cl_2 \longrightarrow S_2Cl_2$$

$$S_2Cl_2 + Cl_2 \longrightarrow 2SCl_2$$

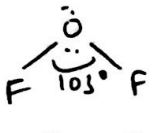
(saturate)



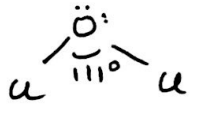
Te → sp^3



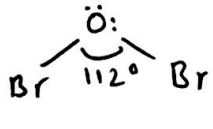
S → sp^3



O - sp^3



O → sp^3



O - sp^3

- In OCl_2 & OBr_2, due to the bulkier size of halogens, the bond angle is more than tetrahedral bond angle.

- $H_2Sn + 2SCl_2 \longrightarrow S_{(n+2)}Cl_2 + 2HCl$

- SCl_2 (dark red liquid) is used in the manufacture of mustard gas

3. Tetrahalides (MX_4)

1st ES

SF_4, SCl_4

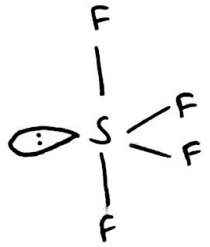
SeF_4, $SeCl_4$, $SeBr_4$

TeF_4, $TeCl_4$, $TeBr_4$, TeI_4

PoF_4, $PoCl_4$, $PoBr_4$, PoI_4

Prep:

- $S + F_2$ (diluted with N_2) $\longrightarrow SF_4$ (since F_2 is OA, if it is not diluted, it gives SF_6)
- $S + 4CoF_3 \longrightarrow SF_4 + 4CoF_2$
- $3SCl_2 + 4NaF \longrightarrow SF_4 + S_2Cl_2 + 4NaCl$
- $SeCl_4 + 4AgF \longrightarrow SeF_4 + 4AgCl$
- $2SeF_4 + TeO_2 \longrightarrow TeF_4 + 2SeOF_4$



$S \longrightarrow sp^3d$ (1st ES)

see-saw

SF_4 can act as LA & LB

- $SF_4 + 2F^- \longrightarrow SF_6^{2-}$ (F^-: LB)
- $SF_4 + BF_3 \longrightarrow [F_4S \longrightarrow BF_3]$ (BF_3: LA)

- Thermal stability: SF_4 (gas) > SeF_4 (liquid) > TeF_4 (solid)

- Hydrolysis:

$$SF_4 + 2H_2O \longrightarrow SO_2 + 4HF$$

$$SCl_4 + 4H_2O \longrightarrow S(OH)_4 + 4HCl$$

$$\downarrow$$

$$H_2SO_3 + 2H_2O$$

- SF_4 & SeF_4 are good fluorinating agents

$CH_3COOH \xrightarrow{SF_4} CH_3-CF_3$

$ROH \xrightarrow{SF_4} RF$

$CH_3CHO \xrightarrow{SeF_4} CH_3-CHF_2$

$R_2CO \xrightarrow{SeF_2} R_2CF_2$

$BCl_3 + SF_4 \longrightarrow BF_3 + SCl_2 + S$

~~$I_2O_5 + 3SF_4 \longrightarrow 2IOF_3 + 3SOF_2$~~

$5SF_4 + I_2O_5 \longrightarrow 2IF_5 + 5SOF_2$

4. Hexahalides (MX_6)

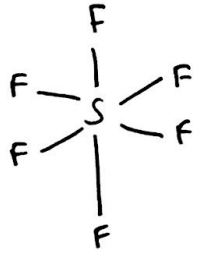
2nd ES

SF_6

SeF_6

TeF_6

Prep: $S + 3F_2 \longrightarrow SF_6$



Spherical symmetry (all S–F bonds are exactly equal)

octahedral)

$S \rightarrow sp^3d^2$ (2nd ES)

- SF_6 is chemically inert and resistant to hydrolysis.

Reason: Steric crowding of 6 F results in S being hindered.

- SF_6 has high dielectric constant.

- SF_6 - gaseous insulation

  Used in high voltage transformers & switch gears

- SF_6, SeF_6, TeF_6 – colourless gases

- Stability of $SF_6 > SeF_6 > TeF_6$

- Extent of hydrolysis : $SF_6 < SeF_6 < TeF_6$

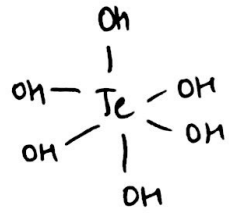
  ↓

  no hyd.

$$TeF_6 + 6H_2O \longrightarrow Te(OH)_6 + 6HF$$

(or)

$H_2TeO_4 \cdot 2H_2O$



~~Basicity = 6~~

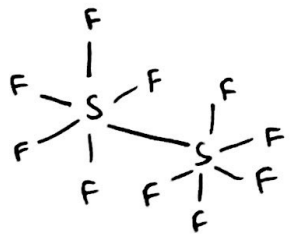
Basicity = 2

- TeF_6 acts as LA and can extend coordination number beyond 6.

$$TeF_6 + F^- \longrightarrow TeF_7^-$$

$$TeF_6 + 2F^- \longrightarrow TeF_8^{2-}$$

- S_2F_{10} $\quad S \rightarrow sp^3d^2$



Max. no. of atoms in a plane = 8

Oxo acids :

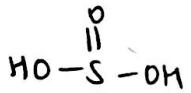
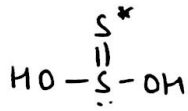
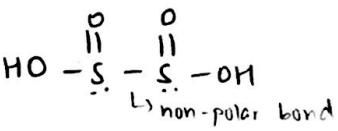
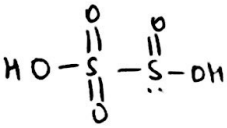
- $MO_2 + H_2O \longrightarrow H_2MO_3$ (ous acids)

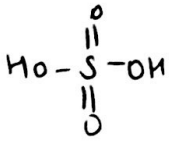
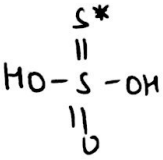
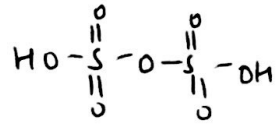
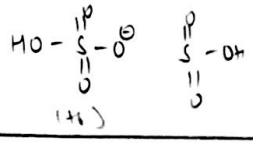
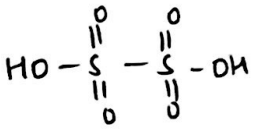
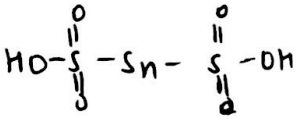
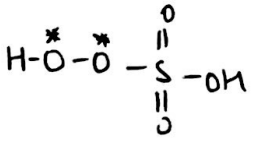
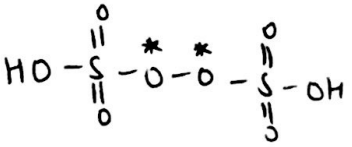
Acidic strength of $H_2SO_3 > H_2SeO_3 > H_2TeO_3$

- $MO_3 + H_2O \longrightarrow H_2MO_4$ (-ic acids)

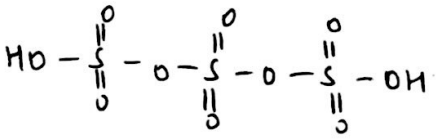
Acidic strength of $H_2SO_4 > H_2SeO_4 > H_2TeO_4$

Oxo-acids of Sulphur

Series - oxo acid	Formula	Structure	Individual O.S	Avg. OS
I: Sulphurous acid series				
1. Sulphurous acid	H_2SO_3		+4	+4
2. Thio sulphurous acid	$H_2S_2O_2$		(-2)* (+4)	+1
3. Di thionous acid	$H_2S_2O_4$		(+3) (+3)	+3
4. Pyro sulphurous acid (Disulphurous acid)	$H_2S_2O_5$		(+5) (+3)	+4

Series - oxo acid	Formula	Structure	Individual OS	Avg OS
II. Sulphuric acid series				
1. Sulphuric acid	H_2SO_4		+6	+6
2. Thio sulphuric acid	$H_2S_2O_3$		(-2)* (+6)	+2
3. Pyro sulphuric acid (Disulphuric acid)	$H_2S_2O_7$	 	(+6) (+6)	+6
III. Thionic acid series.				
1. Dithionic acid (known only in soln)	$H_2S_2O_6$		(+5) (+5)	+5
2. Polythionic acid	$H_2S_{(n+2)}O_6$ (n = 0 to 10)		(+5) (0) (+5)	$\frac{10}{n+2}$
IV. Peroxo acid series				
1. Peroxy monosulphuric acid (Caro's acid)	H_2SO_5		(+6)	+6
2. Peroxy di sulphuric acid (Marshall's acid)	$H_2S_2O_8$		(+6) (+6)	+6

- All oxo acids of Sulphur are dibasic and S is in sp^3 hbd.
- All π-bonds are pπ - dπ
- The oxo anions of sulphur have lesser tendencies to polymerize due to strong pπ - dπ bonds.
- SO_3 is called sulphuric annydride.
- Tri sulphuric acid ($H_2S_3O_{10}$)



All S in +6 state

Oleum

Oleum % / Percentage wt by H_2SO_4

It is the mass of pure H_2SO_4 produced by the sufficient dilution of 100g of oleum.

Ex: 109 % oleum = 100 g oleum ($H_2SO_4 + SO_3$) upon dilution produces 109g of pure H_2SO_4

Wt. of water added = 9 g

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

80g ← 18g

40g 9g

$$\% \text{ free } SO_3 = \frac{40}{100} \times 100 = 40\ \%$$

- 118% oleum → 80% free SO_3
- 122.5% oleum → 100% free SO_3

Oleum % should always be less than 122.5.

$H_2S_2O_6$

- $H_2S_2O_6$ is known only in solution.

SO_2

- Forms hydrate - $SO_2 \cdot 6H_2O$
- BP = -10°C
- MP = -75.5°C
- Colourless suffocating gas

- $SOCl_2$ & SO_2Cl_2 are colourless fuming liquids
- SOF_2 reacts slowly with H_2O
  SO_2F_2 doesn't react with water

Prep:

1. $S + O_2 \longrightarrow SO_2$

2. Roasting:

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

3. Treating sulphites with dil. acid

$$Na_2SO_3 + \underset{(dil)}{2HCl} \longrightarrow 2NaCl + SO_2 + H_2O$$

$$NaHSO_3 + \underset{(dil)}{HCl} \longrightarrow NaCl + SO_2 + H_2O$$

4. $Cu + 2H_2SO_4 \text{ (conc)} \longrightarrow CuSO_4 + SO_2 + 2H_2O$

5. $FeSO_4 \longrightarrow Fe_2O_3 + SO_2 + SO_3$

6. $CaSO_4 + C \longrightarrow CaO + SO_2 + CO_2$

7. $Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + SO_2 + S + H_2O$ (with dil acids, SO_2 & S are produced)

8. $MnO_2 + H_2SO_4 \text{ (conc)} \longrightarrow MnSO_4 + SO_2 + H_2O$

9. $SOCl_2 + H_2O \longrightarrow SO_2 + 2HCl$

Chemical properties:

1. $2SO_2 + O_2 \xrightarrow[\Delta]{V_2O_5} 2SO_3$

2. With NaOH

$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$

$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3$

3. With lime water (behaves like CO_2) - turns milky which disappears when excess SO_2 is sent.

$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 \downarrow + H_2O$
(Milky ppt)

$CaSO_3 + H_2O + SO_2 \longrightarrow Ca(HSO_3)_2$
soluble
(milkiness disappears)

- Same observation even with baryta water ($Ba(OH)_2$)

4. $SO_2 + Mg \longrightarrow MgS + MgO$

Though SO_2 doesn't support combustion, Mg continues burning due to the heat liberated as a result of high LE of MgS & MgO

- $SO_2 + C \longrightarrow CO_2 + S$

5. Bleaching action

- SO_2 bleaches in the presence of moisture.
- Bleaches by reduction
- $$SO_2 + 2H_2O \rightleftharpoons H_2SO_4 + 2(H)$$
- Temporary bleaching agent
- SO_2 is powerful bleaching agent in alkaline med as alkali consumes H_2SO_4.

6. SO_2 is a powerful reducing agent.

- $SO_2 + 2H_2O + X_2 \longrightarrow HX + H_2SO_4$

  (X= Cl, Br, I)
- $SO_2 + 2FeCl_3 + 2H_2O \longrightarrow 2FeCl_2 + 2HCl + H_2SO_4$

  (yellow) (light green)
- * $SO_2 + H_2O_2 \longrightarrow H_2SO_4$
- $3SO_2 + O_3 \longrightarrow 3SO_3$
- * $5SO_2 + 2IO_3^- + 4H_2O \xrightarrow{+2H^+} I_2 + 5H_2SO_4$
- $SO_2 + MnO_4^- + H_2O \longrightarrow Mn^{+2} + SO_4^{2-} + H^+$
- $K_2Cr_2O_7 + SO_2 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$
- * $SO_2 + NO_2 \longrightarrow SO_3 + NO$

- $SO_2 + 2SnCl_4 + HCl \longrightarrow 2SnCl_2 + H_2SO_4$

7. SO_2 is a mild oxidant.

- $SO_2 + H_2S \longrightarrow S + H_2O$
- $SO_2 + CO \longrightarrow CO_2 + S$
- $SO_2 + 2SnCl_2 + 4HCl \longrightarrow 2SnCl_4 + S + 2H_2O$
- $SO_2 + 2Hg_2Cl_2 + 4HCl \longrightarrow 4HgCl_2 + S + 2H_2O$

* Other reactions:

- $SO_2 + Cl_2 \xrightarrow{\text{charcoal}} SO_2Cl_2$ (sulphuryl chloride)
- $SO_2 + PCl_5 \longrightarrow POCl_3 + SOCl_2$ (thionyl chloride / sulphonyl chloride)
- $3SO_2 + 4K \longrightarrow K_2SO_3 + K_2S_2O_3$

Uses:

- Used in manufacture of H_2SO_4 & paper from wood pulp & food preservatives
- Refining of petroleum and sugar
- Disinfectant
- Fungicide
- Refrigerant in the form of liquid SO_2
- Antichlor
- A very good non-aqueous solvent (undergoes self ionization)

$SO_2 + SO_2 \rightleftharpoons SO^{+2} + SO_3^{2-}$

SO_3

Prep:

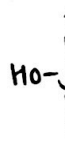
1. $2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$

* 2. $Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + SO_3$

3. H_2SO_4 (conc) + P_4O_{10} (dehydrating agent) $\longrightarrow SO_3 + H_3PO_4 / HPO_3$ (depends on conditions)

Chem properties

1. $SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$

* 2. $SO_3 + HCl \longrightarrow$  (or) $HO-SO_2-Cl$

3. $SO_3 + 2HBr \longrightarrow SO_2 + Br_2 + H_2O$

* 4. $SO_3 + H_2SO_4 + NH_2CONH_2 \longrightarrow 2\,NH_2\text{-}SO_2\text{-}OH + CO_2$ (Sulphamic acid)

5. $SO_3 + PCl_5 \longrightarrow POCl_3 + SO_2 + Cl_2$

6. $2SO_3 + S \longrightarrow 3SO_2$

7. $5SO_3 + 2P \longrightarrow P_2O_5 + 5SO_2$

- SO_3 should not be dissolved in H_2O to get H_2SO_4.

Reason: The rxn. is highly exothermic & gives off H_2SO_4 vapours

H_2S

Prep:

1. $FeS + 2HCl \longrightarrow FeCl_2 + H_2S$

2. $Sb_2S_3 + 6HCl \longrightarrow 2SbCl_3 + 3H_2S$

Chem properties

1. H_2S is a good reductant.

- $H_2S + X_2 \longrightarrow 2HX + S \quad (X = Cl, Br)$
- $H_2S + 4F_2 \longrightarrow SF_6 + 2HF$
- $H_2S + FeCl_3 \longrightarrow FeCl_2 + S + 2HCl$
- $H_2S + O_3 \longrightarrow H_2O + S + O_2$
- $H_2S + H_2O_2 \longrightarrow H_2O + S + O_2$
- $H_2S + SO_2 \longrightarrow S + H_2O$
- $H_2S + MnO_4^- + H^+ \longrightarrow Mn^{2+} + S + H_2O$
- $H_2S + K_2Cr_2O_7 + H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + S + K_2SO_4 + H_2O$

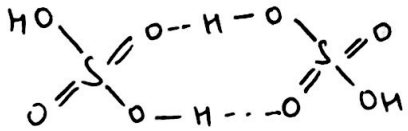
- $H_2S + HNO_3 \longrightarrow NO_2 + S + H_2O$
- $H_2S + H_2SO_4 \longrightarrow SO_2 + S + H_2O$

Uses:

- Lab reagent
- Metal sulphides are used in paint industry
- A good reducing agent.
- On passing excess of H_2S through $(NH_4)_2S$, Yellow ammonium sulphide is formed

H_2SO_4

- Colourless viscous liquid & less volatile due to H-bonding



- Azeotropic composition : 98.3% H_2SO_4 + 1.7% H_2O

  density of azeotropic mix. at 298 K = 1.84 g/cc

- BP = 590K
- FP = 283K

- called 'oil of vitriol'
- Sulphuric acid is ~~dil~~ diluted by adding H_2SO_4 to H_2O but not H_2O to H_2SO_4.

  Reason: H_2SO_4 forms hydrates having general formula $H_2SO_4 \cdot nH_2O$ which is highly exothermic.

Manufacture

By Lead chamber process

Catalyst: oxides of N

$$2NO + O_2 \longrightarrow 2NO_2$$

$$SO_2 + NO_2 \longrightarrow SO_3 + NO$$

$$SO_3 + H_2SO_4 \longrightarrow ~~H_2SO_4~~ \; H_2S_2O_7$$

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

NO & NO_2 absorbed by $(NH_4)_2SO_4$

$$NO + NO_2 + (NH_4)_2SO_4 \downarrow$$

$$N_2 + H_2SO_4 + H_2O$$

Contact's process

- Principle eq: $2SO_2 + O_2 \rightleftharpoons 2SO_3 \qquad \Delta H = -196 \text{ kJ}$
- Optimum high P = 2 bar
- Optimum low T = 700 - 723 K

*. Catalyst : V_2O_5 (or) Pt

V_2O_5 is preferred to Pt (V_2O_5 is cheaper & Pt is readily poisoned)

- Catalytic poison : As_2O_3
  (Impurity)

As_2O_3 is removed by gelatinous $Fe(OH)_3$ or. $Fe_2O_3 \cdot xH_2O$

1. Pyrite burner

$$S + O_2 \longrightarrow SO_2$$

$$FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$$

2. Dusting chamber

Dust particles are removed.

3. Scrubber:

Gases are treated with water.

4. Drying tower:

Gases are dried by conc. H_2SO_4.

5. Arsenic purifier

As impurity is eliminated

6. Catalytic chamber | oxidation chamber

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

7. Absorption tower

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

SO_3 is absorbed in H_2SO_4

8. Dilution tower

Oleum is diluted with H_2O

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

Chemical properties

1. $H_2SO_4 + NaOH \longrightarrow NaHSO_4 + H_2O$

$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$

2. H_2SO_4 (dil) $+ Na_2CO_3 \longrightarrow Na_2SO_4 + CO_2 + H_2O$

H_2SO_4 (dil) $+ NaHCO_3 \longrightarrow Na_2SO_4 + CO_2 + H_2O$

3. H_2SO_4 displaces more volatile acid from salts since H_2SO_4 is less volatile.

- $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$
- $KNO_3 + H_2SO_4$ (conc) $\longrightarrow KHSO_4 + HNO_3$
- $KNO_2 + H_2SO_4$ (conc) $\longrightarrow KHSO_4 + HNO_2$
- $NaCl + H_2SO_4$ (conc) $\longrightarrow NaHSO_4 + HCl$
- $CaC_2O_4 + H_2SO_4$ (dil) $\longrightarrow H_2C_2O_4 + CaSO_4$
- $CH_3COONa + H_2SO_4$ (conc) $\longrightarrow CH_3COOH + NaHSO_4$
- $Ca_3(PO_4)_2 + H_2SO_4 \longrightarrow CaSO_4 + H_3PO_4$

4. Dil. H_2SO_4

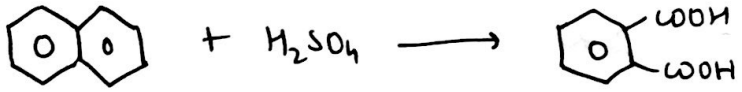
- $Zn + H_2SO_4 \text{ (dil)} \longrightarrow ZnSO_4 + H_2\uparrow$
- $Fe + H_2SO_4 \text{ (dil)} \longrightarrow FeSO_4 + H_2\uparrow$
- $Cu, Ag, Au, Hg, Pt + H_2SO_4 \text{ (dil)} \longrightarrow$ No rxn

5. With conc. H_2SO_4

$$Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$$

$$Ag + H_2SO_4 \longrightarrow Ag_2SO_4 + SO_2 + H_2O$$

6. Conc. H_2SO_4 is a mild oxidant.

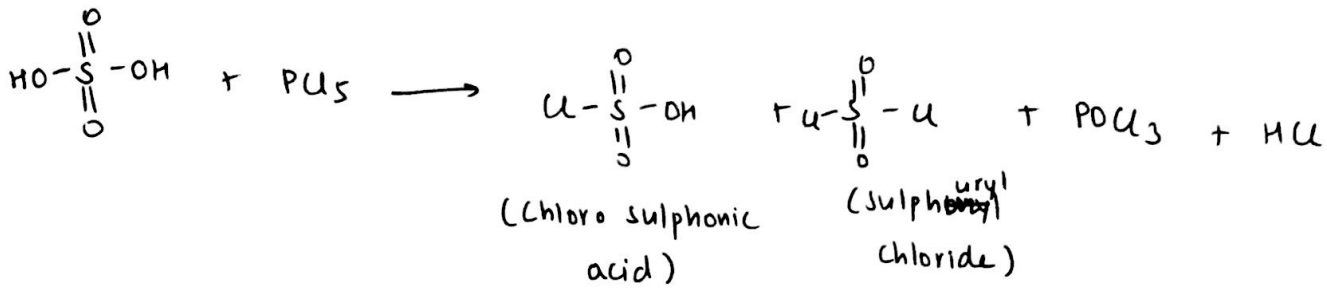
- $H_2SO_4 + C \longrightarrow CO_2 + SO_2 + H_2O$
- $H_2SO_4 + P \longrightarrow H_3PO_4 + SO_2 + H_2O$
- $H_2SO_4 + S \longrightarrow SO_2 + H_2O$
- * 

7. With $K_4[Fe(CN)_6]$

a) $K_4[Fe(CN)_6] + H_2SO_4 \text{ (conc)} + H_2O \longrightarrow K_2SO_4 + FeSO_4 + (NH_4)_2SO_4 + \boxed{CO}\uparrow$

b) $K_4[Fe(CN)_6] + H_2SO_4 \text{ (dil)} \longrightarrow K_2SO_4 + FeSO_4 + \boxed{HCN}$

8. With PCl_5: -OH replaced by -Cl



9. Dehydrating agent

a) Carbonydrates + conc. H_2SO_4 ⟶ charring occurs due to formation of C

$$C_{12}H_{22}O_{11} \xrightarrow[-11\,H_2O]{\text{conc. } H_2SO_4} 12\,C$$

$$C_6H_{12}O_6 \xrightarrow[-6\,H_2O]{\text{conc. } H_2SO_4} 6\,C$$

b) $$H_2C_2O_4 \xrightarrow{\text{conc. } H_2SO_4} CO + CO_2 + H_2O$$

$$HCOOH \xrightarrow{\text{conc. } H_2SO_4} CO + H_2O$$

Uses:

- Manufacture of fertilizers $(NH_4)_2SO_4$, superphosphate of lime
- Manufacture of nitroglycerine, gun cotton, TNT, picric acid
- Petroleum refining
- Manufacture of dyes, drugs
- Textile & paper industries
- Tanning industries
- Pickling agent

- Lead storage battery (Eq. wt of H_2SO_4 = 98)
- Manufacture of paints & pigments
- Dehydrating agent.

Hypo Sodium thiosulphate pentahydrate $Na_2S_2O_3 \cdot 5H_2O$

- White crystalline efflorescent solid.
- Highly soluble in water & hence forms super saturated solutions.
- ***

$$Na_2S_2O_3 \xrightarrow{\Delta} Na_2S_5 + Na_2SO_4$$

Prep:

1. Spring's rxn

$$Na_2S + Na_2SO_3 + I_2 \longrightarrow Na_2S_2O_3 + 2NaI$$

2. $Na_2SO_3 + S \xrightarrow{\text{boiled}} Na_2S_2O_3$

*
3. $2Na_2S + 3SO_2 \longrightarrow 2Na_2S_2O_3 + S$

4. $Na_2SO_4 + C \longrightarrow Na_2S + CO$

$2Na_2S + 3SO_2 \longrightarrow 2Na_2S_2O_3 + S$

5. $Na_2S + Na_2CO_3 + SO_2 \longrightarrow Na_2S_2O_3 + CO_2$

**
6. $NaOH + S \longrightarrow Na_2S / Na_2S_5 + Na_2S_2O_3 + H_2O$

Chem properties

1. With dil. HCl

$$Na_2S_2O_3 + 2HCl \longrightarrow SO_2\uparrow + S\downarrow + 2NaCl + H_2O$$

2. With $AgNO_3$

a) With dil. $Na_2S_2O_3$

$$2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3\downarrow + 2NaNO_3$$

(white ppt)

$$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S\downarrow + H_2SO_4$$

(black ppt)

b) With conc. $Na_2S_2O_3$

$$2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3\downarrow + 2NaNO_3$$

(white ppt)

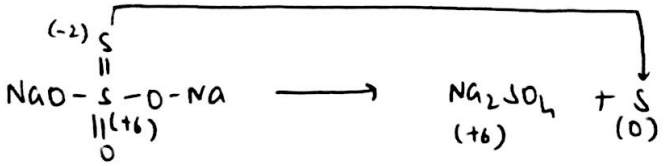
$$Ag_2S_2O_3 + Na_2S_2O_3 \longrightarrow 2Na_3[Ag(S_2O_3)_2]$$

soluble complex

**

3. With I_2

$$Na_2S_2O_3 + I_2 + H_2O \longrightarrow Na_2SO_4 + S + 2HI$$



Eq. wt of hypo = $\frac{M}{2}$

- Hypo is used to remove excess Cl_2 on fabric during bleaching. So it is called 'anti-chlor'.

4. With $FeCl_3$

$$Fe^{+3} + S_2O_3^{2-} \longrightarrow \underset{\text{violet}}{[Fe(S_2O_3)_2]^-} \xrightarrow{Fe^{3+}} \underset{\text{(green)}}{2Fe^{2+}} + S_4O_6^{2-}$$

5. With I_2

$$\underset{(+2)}{2Na_2S_2O_3} + I_2 \longrightarrow 2NaI + \underset{(+2.5)}{Na_2S_4O_6}$$

$0.5 \times 2 = 1e^-$

Eq. wt of hypo $= \frac{M}{1} = M$

*

. Iodometry:

- $2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + I_2 + 2K_2SO_4$

  2 moles $CuSO_4$ = 1 mol I_2

- $H_2O_2 + 2KI + H_2SO_4 \longrightarrow I_2 + K_2SO_4 + 2H_2O$

- $CaOCl_2 + CH_3COOH \longrightarrow Ca(CH_3COO)_2 + Cl_2 + H_2O$ (geq. of $CaOCl_2$ = geq. of Cl_2 = geq. of I_2)

  $Cl_2 + 2KI \longrightarrow 2KCl + \boxed{I_2}$

Gm. eq. of I_2 = Gm eq. of $Na_2S_2O_3$

Uses:

- Hypo is used in iodometry.
- Anti-chlor
- Anti-septic & Germicide
- Extraction of metals like Cu, Ag (complex formation)
- * Photography development

$$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

- ** $Cu^{2+} + Na_2S_2O_3 \longrightarrow Na_4[Cu_6(S_2O_3)_5]$

Ozone

- Deep blue gas
  Deep blue liquid
  Violet solid
- FP = 80 K
  BP = 161 K
- 1.6 times heavier than air
- Above 100 ppm causes headaches and nausea
- *** Slightly soluble in water but highly soluble in CCl_4, glacial acetic acid & turpentine oiland cinnamon oil.

- Thermodynamically less stable.

- $3O_2 \rightleftharpoons 2O_3$ (g) (g) $\quad \Delta H = +284.5\ kJ$

  $\Delta H = +ve$

  $\Delta S = -ve$

  $\Delta G = +ve$

Formation of O_3 is endothermic

- $2O_3 \rightleftharpoons 3O_2$ (g) (g) $\quad \Delta H = -284.5\ kJ$

  $\Delta H = -ve$

  $\Delta S = +ve$

  $\Delta G = -ve$

- For $2O_3 \rightleftharpoons 3O_2$

$$R = k\frac{[O_3]^2}{[O_2]}$$

$O_3 \rightleftharpoons O_2 + (O)$

$O_3 + (O) \longrightarrow 2O_2$ RDS

- $2O_3 \rightleftharpoons 3O_2$

$t=0$	V_0	0
$t = t_{eq}$	$V_0 - 2x$	$3x$
$t = \infty$	0	$\frac{3V_0}{2}$ (if rxn it allowed to complete)

Prep

1. $2F_2 + 2H_2O \longrightarrow 4HF + O_2$

   $3F_2 + 3H_2O \longrightarrow 6HF + O_3$

   $5F_2 + 5H_2O \longrightarrow 10HF + O_3 + O_2$

   $O_3 + O_2$ → Ozonized oxygen

- The amount of O_3 in a gas mix. is estimated by passing it through aq. KI solution in the presence of borate buffer (pH = 9.2)

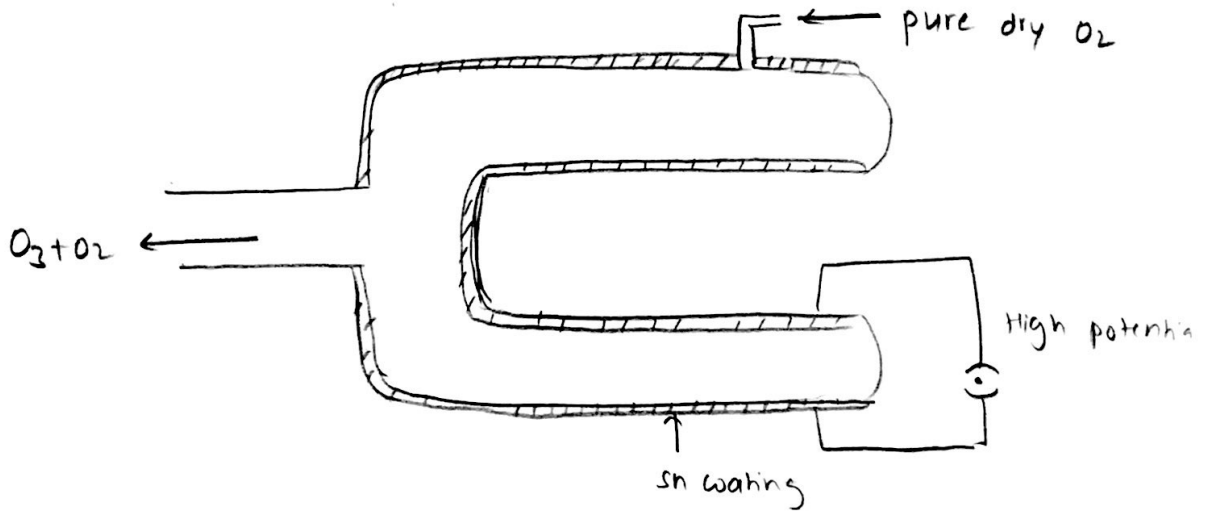
- Depletion of ozone layer is due to oxides of nitrogen (mainly NO) and halide radicals.

Manufacture of Ozone

- Ozone is manufactured by the silent electric discharge of pure, dry, cold oxygen in ozonizer. (without ↓ spark)

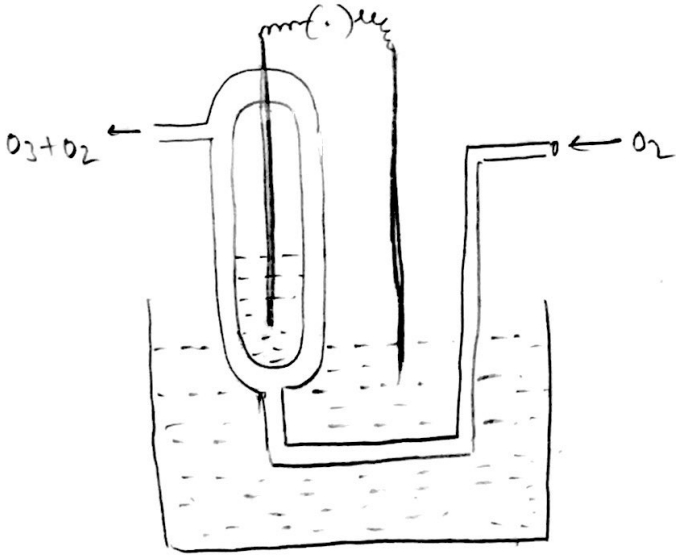
- In ozonizer, 10% of O_2 is converted to O_3. The mixture of O_2 & O_3 thus obtained is called ozonized oxygen.

Siemen's ozonizer



O_2 undergoes silent electric discharge in the annular space

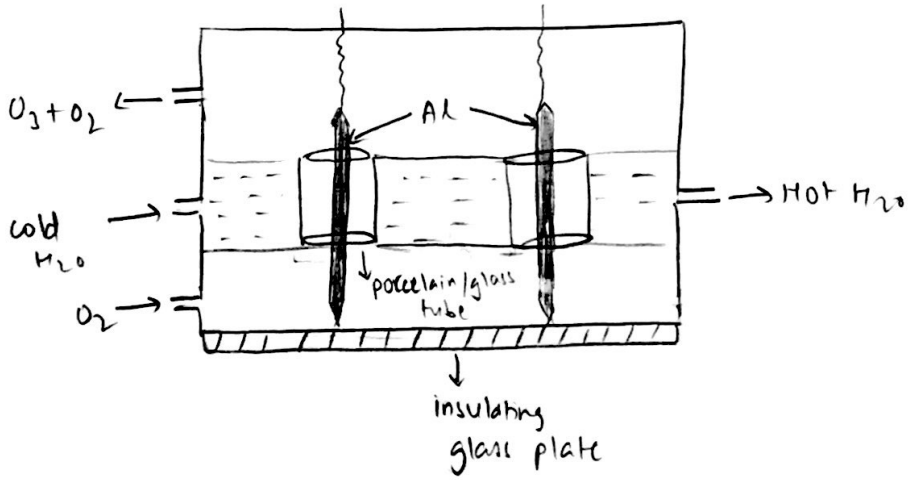
Brodie's ozonizer:



Electrolytes: dil. H_2SO_4
(or)
Aq. $CuSO_4$

Electrodes: Cu

Siemen - Halske's ozonizer



Oxidising properties of O_3

- O_3 is a powerful oxidant next to F_2
- $O_3 \longrightarrow O_2 + (O)$
- $PbS + 4(O) \longrightarrow PbSO_4$
  $4O_3 \longrightarrow 4O_2 + 4(O)$

- $NaNO_2 \longrightarrow NaNO_3$
- $Na_3AsO_3 \longrightarrow Na_3AsO_4$
- $Na_2SO_3 \longrightarrow Na_2SO_4$

$PbS + 4O_3 \longrightarrow PbSO_4 + 4O_2$ ✓

$PbS + 2O_3 \longrightarrow PbSO_4 + O_2$ ✗

*. $MS + 4O_3 \longrightarrow MSO_4 + 4O_2$ (M= Cu, Pb, Zn, Cd)

*. $O_3 + 2KI + H_2O \longrightarrow I_2 + 2KOH + O_2$

*. $3O_3 + KI \longrightarrow KIO_3 + 3O_2$

$4O_3 + KI \longrightarrow KIO_4 + 4O_2$

. $I_2 + H_2O + 5O_3 \longrightarrow HIO_3 + 5O_2$

$I_2 + H_2O + 5(O) \longrightarrow 2HIO_3$

$I_2 + \underset{\text{ozone}}{\text{dry}} \rightarrow I_4O_9$

$I_2 + \underset{\text{ozone}}{\text{moist}} \longrightarrow HIO_3$

*. $I_2 + O_3 \longrightarrow I_4O_9 + O_2$

(Ionic)

Exists as $I(IO_3)_3 \longrightarrow I^{+3} + 3IO_3^-$

Has metallic properties

(Yellow powder)

. $2FeSO_4 + O_3 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + H_2O + O_2$

. $2HX + O_3 \longrightarrow X_2 + O_2 + H_2O$

(X = Cl, Br)

. $H_2S + O_3 \longrightarrow S + H_2O + O_2$

. $P + H_2O + 5O_3 \longrightarrow H_3PO_4 + 5O_2$

$2P + 3H_2O + 5(O) \longrightarrow 2H_3PO_4$

$$S + H_2O + 3O_3 \longrightarrow H_2SO_4 + 3O_2$$

$$S + H_2O + 3(O) \longrightarrow H_2SO_4$$

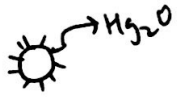
$$2KOH + 5O_3 \longrightarrow 2KO_3 + H_2O + 5O_2$$

$$2KOH + 5(O) \longrightarrow 2KO_3 + H_2O$$

$$2K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$$

$$2K_4[Fe(CN)_6] + O_3 + H_2O \longrightarrow 2K_3[Fe(CN)_6] + 2KOH + O_2$$

Tailing of mercury



$$2Hg + O_3 \longrightarrow \boxed{Hg_2O} + O_2$$

If H_2O_2 is used, HgO forms

$$Hg + H_2O_2 \longrightarrow HgO + H_2O$$

- In the presence of O_3, Hg loses its soft meniscus and sticks to the surface of glass. This is called tailing of mercury.

Bleaching action

$$O_3 \longrightarrow O_2 + (O)$$

- Bleaches by oxidation
- *. Dry bleaching agent.
- Perm. Temporary bleaching agent

SO_2 → bleaches by reduction

Cl_2 → permanent bleaching agent

O_3 → Dry bleaching agent.

Oxidising bleaching agents are permanent

***

- In the above ~~oxidati~~ oxidizing properties, only one oxygen atom per ~~oxy~~ ozone molecule is consumed.

But in the following rxns, all oxygens of O_3 are completely consumed.

- $3SO_2 + O_3 \longrightarrow 3SO_3$
- $3SnCl_2 + 6HCl + O_3 \longrightarrow 3SnCl_4 + 3H_2O$

· Reducing properties

$O_3 + (O) \longrightarrow 2O_2$

- $Ag_2O + O_3 \longrightarrow 2Ag + 2O_2$
- $BaO_2 + O_3 \longrightarrow BaO + 2O_2$
- $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$

→ Mutual reductions

· Tarnishing of Ag

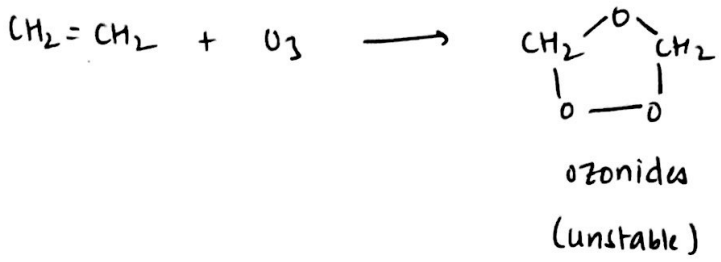
$2Ag + O_3 \longrightarrow Ag_2O + O_2$ (Oxidation)

(Bright)

$Ag_2O + O_3 \longrightarrow 2Ag + 2O_2$ (Reduction)

(tarnished)

- Addition reactions:



ozonides
(unstable)

~~Uses~~

Tests for O_3

- Tails Hg
- Starch iodide paper → blue
- Benzidine paper → brown
- Tarnishes silver

Uses:

- Oxidant, reductant, bleaching agent
- Disinfectant, germicide
- Oxidant in rocket fuels
- Purification of air
- Removal of bad odours from kitchen
- Sterilization of water.

Hydrogen Peroxide

Refer to Hydrogen & its compounds

- Na_2O_2 / BaO_2 + dil. acid $\longrightarrow$ H_2O_2

  Best with H_3PO_4

  HNO_3 oxidises H_2O_2 to O_2

- BaO_2 + H_2O + CO_2 $\longrightarrow$ H_2O_2 + $BaCO_3\downarrow$

  (slurry)

- 2-Ethyl anthraquinol + O_2 $\longrightarrow$ H_2O_2 + 2-Ethyl anthraquinone

  Ni/H_2

  (Auto oxidation)

- Electrolysis of 50% H_2SO_4 using high current density produces $H_2S_2O_8$ which upon distillation gives H_2O_2

$$2H_2SO_4 \longrightarrow 2H^+ + 2HSO_4^-$$

Anode: $2HSO_4^- \longrightarrow H_2S_2O_8 + 2e^-$

Cathode: $2H^+ + 2e^- \longrightarrow H_2\uparrow$

$[H^+]\downarrow \Rightarrow pH\uparrow$

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$$

$$H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2$$

$$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$$

- Insted of H_2SO_4 solution, NH_4HSO_4 may be used.

$$2NH_4HSO_4 \longrightarrow 2H^+ + 2NH_4SO_4^-$$

Chemical properties:

1. Oxidising properties

$H_2O_2 \longrightarrow H_2O / OH^-$

Oxidises:

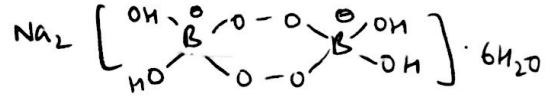
- $PbS \longrightarrow PbSO_4$ (used to restore colour to paint)
  (black) (white)
- $NaNO_2 \longrightarrow NaNO_3$
- $Na_3AsO_3 \longrightarrow Na_3AsO_4$
- $Na_2SO_3 \longrightarrow Na_2SO_4$
- $Fe^{+2} \longrightarrow Fe^{+3}$
- $KI \longrightarrow I_2$
- ~~O_3~~ $H_2S \longrightarrow S$
- $HCHO \longrightarrow HCOOH + \boxed{H_2}$
- $NH_2OH \longrightarrow HNO_3$
- $N_2H_4 \longrightarrow N_2$
- $[Cr(OH)_4]^- + H_2O_2 + OH^- \longrightarrow CrO_4^{2-} + H_2O$
- $CrO_4^{2-} / Cr_2O_7^{2-} + H_2O_2 + H^+ \longrightarrow CrO_5$
  (blue peroxide)
  fades in acidic med.
  ($CrO_5 + H^+ \longrightarrow Cr^{+3} + O_2 \uparrow$)

$2HCHO + H_2O_2 \rightarrow 2HCOOH + H_2$

- $K_4[Fe(CN)_6] \xrightarrow[H_2O_2]{H^+} K_3[Fe(CN)_6]$

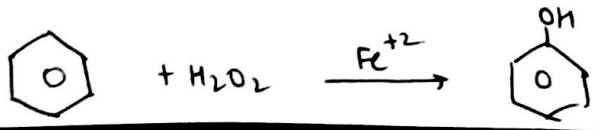
- $H_3BO_3 + H_2O_2 \longrightarrow HOOB(OH)_3$

$HOOB(OH)_3 + NaOH + H_2O_2$



Sodium peroxo borate
(tetrahedral at B)

- $Mn^{+2} + H_2O_2 + OH^- \longrightarrow MnO_2 + H_2O$



(Fe^{+2} in H_2O_2 is Fenton's reagent

2. Reducing properties

$$H_2O_2 \longrightarrow O_2$$

- $KIO_4 + H_2O_2 \longrightarrow KIO_3 + H_2O + O_2$
- $NaOCl + H_2O_2 \longrightarrow NaCl + H_2O + O_2$
- $Ag_2O \rightarrow Ag$
- $O_3 \rightarrow O_2$
- $PbO_2 \longrightarrow PbO$

* . $X_2 \longrightarrow HX \quad (X = Cl, Br)$ H_2O_2 can't react with HX to give X_2

- $MnO_2 + H_2SO_4 + H_2O_2 \longrightarrow MnSO_4 + H_2O + O_2$

*** $2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2$

gm. eq. of $KMnO_4$ = gm. eq. of H_2O_2 = $\frac{1}{2}$ gm eq. of O_2

*

- $2KMnO_4 + H_2O_2 \longrightarrow MnO_2 + KOH + O_2$ (mild, alk. med)
- $2K_3[Fe(CN)_6] + 2KOH + H_2O_2 \longrightarrow 2K_4[Fe(CN)_6] + 2H_2O + O_2$

$$K_4[Fe(CN)_6] \xrightarrow[H_2O_2]{H^+} K_3[Fe(CN)_6]$$

$$K_3[Fe(CN)_6] \xrightarrow[H_2O_2]{OH^-} K_4[Fe(CN)_6]$$

Concentration methods

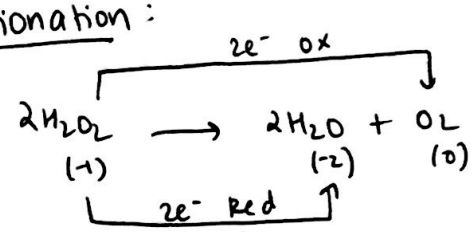
Volume strength (Vs):

- It is the volume of O_2 liberated by the decomposition of 1 mL or 1L of H_2O_2 at STP.

$$V_{O_2} = V_{S(H_2O_2)} \times V_{(H_2O_2)}$$

- $\%(W/V) = 0.3036\ Vs$
- $M = \frac{Vs}{11.2}$
- $N = MX2 = \frac{Vs}{5.6}$

Disproportionation:



$$E_{H_2O_2\ (oxidant)} = \frac{34}{2}$$

$$E_{H_2O_2\ (reductant)} = \frac{34}{2}$$

$$E_{H_2O_2\ (Disproportionation)} = \frac{34}{2} + \frac{34}{2} = 34$$

*

- 100 volume H_2O_2 = Perhydral

$$\%\left(\frac{W}{V}\right) = 30.36\%$$

$$M = \frac{100}{11.2} = 8.93\ M$$

$$N = 17.86\ N$$

- Hyperol = Addition compound of (urea + H_2O_2)

  $NH_2CONH_2 \cdot H_2O_2$

Dioxygen

- BP = 90 K
- FP = 55 K
- Non-combustile but supports combustion.
- ★ Due to high ~~BDE~~ Bond energy = 490 kJ, the formation of metal oxide requires initiation.

Prep:

- ★ $KMnO_4 \longrightarrow K_2MnO_4 + O_2 + MnO_2$
- $2KClO_3 \longrightarrow 2KCl + 3O_2$
- $2KNO_3 \longrightarrow 2KNO_2 + O_2$
- $NaNO_3 \longrightarrow NaNO_2 + O_2$
- ★ $K_2Cr_2O_7 \longrightarrow K_2CrO_4 + Cr_2O_3 + O_2$ (Cr_2O_3: green)

- $2H_2O_2 \longrightarrow 2H_2O + O_2$
- $Na_2O_2 + H_2O \longrightarrow NaOH + O_2$ (conc) soln
- $2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + O_2$
- $CaOCl_2 \xrightarrow[\Delta]{CoCl_2} CaCl_2 + \frac{1}{2}O_2$
- $2Ag_2O \xrightarrow{\Delta} 4Ag + O_2$
- $2HgO \xrightarrow{\Delta} 2Hg + O_2$
- $BaO_2 \xrightarrow{\Delta} BaO + O_2$
- $Pb_3O_4 \xrightarrow{\Delta} 3PbO + \frac{1}{2}O_2$
- $3MnO_2 \longrightarrow Mn_3O_4 + O_2$

- In all reducing properties of H_2O_2, O_2 is a byproduct.
- In oxidizing properties of O_3 (except in $2KI + O_3 + H_2O \longrightarrow 2KOH + I_2 + O_2$), O_2 is a byproduct

Chem properties

- Metal $+ O_2 \longrightarrow$ Metal oxide
- Non-metal $+ O_2 \longrightarrow$ Non-metal oxide

Imp:

- $2SO_2 + O_2 \xrightarrow{V_2O_5 / Pt} 2SO_3$
- $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$ (Deacon's process)
- $NH_3 + O_2 \xrightarrow{Rh/Pt} NO + H_2O$

Types of oxides based on nature

1. Acidic oxides:

- Generally, non-metal oxides are acidic.

  Ex: N_2O_5, Cl_2O_7, P_4O_{10}, SO_2, SO_3 etc.

- Some metal oxides are also acidic

  Ex: $\boxed{CrO_3, Mn_2O_7}$, V_2O_5

2. Basic oxides:

- Generally, metal oxides are basic:

  Ex: Na_2O, CaO, SrO, BaO, Fe_2O_3

  CrO, MnO, VO, TiO etc

Lanthanide oxides are basic since lanthanides are as electropositive as 2nd group metals.

****

3. Amphoteric oxides

Metal oxides: BeO, ZnO, Al_2O_3, PbO, PbO_2, SnO, SnO_2

Mn_3O_4, MnO_2, CrO_2, Cr_2O_3, PoO_2

Metalloid oxides: Sb_2O_3, As_2O_3, TeO_2, Ga_2O_3

***

4. Neutral oxides:

N_2O, NO, CO, H_2O

Types of oxides based on oxygen content

1. Normal oxides:

Na_2O, K_2O, Rb_2O, Cs_2O

Al_2O_3, BaO, Fe_2O_3

. Peroxides:

Na_2O_2, K_2O_2, Rb_2O_2, Cs_2O_2

BaO_2, SrO_2, CaO_2

$NaHO_2$, H_2O_2

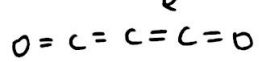
CrOs

3. Superoxides:

KO_2, RbO_2, CsO_2

4. Suboxides

N_2O, C_3O_2



5. Mixed oxides

$Pb_3O_4 \longrightarrow 2PbO + PbO_2$

$Mn_3O_4 \longrightarrow 2MnO + MnO_2$

$Fe_3O_4 \longrightarrow FeO + Fe_2O_3$

Uses:

1. $N_2H_4 + O_2 \longrightarrow$ Rocket fuel
2. $CO_2 + O_2 \longrightarrow$ Treating CO poisoned victims
3. $(He + O_2) \longrightarrow$ Artificial respiration of pneumonia patients.

- H_2S is dried over P_4O_{10}, anh. $CaCl_2$ and fused Al_2O_3 but not conc. H_2SO_4
- $S=S$ is strong with Bond energy 422 kJ/mol

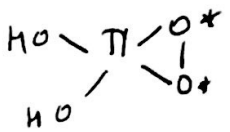
Identification for H_2O_2

1. Converts PbS (black) $\longrightarrow$ $PbSO_4$ (white)
2. Forms blue peroxide with $K_2Cr_2O_7$

3. $TiO_2 + H_2SO_4 \longrightarrow Ti(SO_4)_2 \xrightarrow[+H_2SO_4]{H_2O_2} H_2TiO_4$

pertitanic acid

orange colouration



- $SO_2 + K_2HgCl_4 + H_2O \longrightarrow K_2[Hg(SO_3)_2]$

  ↓ treated with para rosaniline

- Gun powder = $KNO_3 + C + S$

- In lead chamber process, NO & NO_2 gases at the end of rxn are absorbed by $(NH_4)_2SO_4$

$$NO + NO_2 + (NH_4)_2SO_4 \longrightarrow N_2 + H_2SO_4 + H_2O$$

- Glycerol, urea, sodium pyrophosphate, sodium stannate, acetanilide retard the decomposition of H_2O_2

- In alkaline med, H_2O_2 is unstable.

- Metals, rough surfaces, metal oxides, sunlight accelerate the decomposition of H_2O_2

- Super acids- Fluoro sulphuric acid

$$SbF_5 + H_2F_2 \longrightarrow H_2F\,SbF_6$$